



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/GB92/02161 <b>(22) International Filing Date:</b> 23 November 1992 (23.11.92)  <b>(30) Priority data:</b> 9125560.4 30 November 1991 (30.11.91) GB 9212167.2 9 June 1992 (09.06.92) GB  <b>(71) Applicant (for all designated States except US):</b> LAPORTE INDUSTRIES LIMITED [GB/GB]; 3 Bedford Square, London WC1B 3RA (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> BUCK, Malcolm, Johnstone [GB/GB]; 8 Coulton Road, Weates Close, Widnes, Cheshire WA8 0DX (GB). CROFTS, Rhona, Dorothy [GB/GB]; 15 Livingstone Place, Marchmont, Edinburgh EH9 1PE (GB). PURCHASE, Linda, June [GB/GB]; 19 Fairburn Close, Weates Close, Widnes, Cheshire WA8 0EN (GB).		<b>(74) Agent:</b> GREEN, M., C.; Urquhart-Dykes & Lord, 91 Wimpole Street, London W1M 8AH (GB).  <b>(81) Designated States:</b> AU, CA, JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> SYNTHESIS OF SMECTITE CLAY MINERALS  <b>(57) Abstract</b>  A process for the synthesis of a smectite type mineral such as hectorite comprising the formation of a solid reaction product containing the magnesium and silicon values of the hectorite by the precipitation of at least a proportion of the said values under basic conditions to form a precursor and the subsequent treatment of the said precursor under hydrothermal conditions to achieve crystallisation of a product having a hectorite structure and the separation and washing of that product, the process being characterised in that the pH under which the precipitation is conducted is controlled at from 7.5 to 9 or from 9.7 to 10 to improve processing or performance characteristics for example, the washing time, the rate of dispersion, the clarity dispersion, the time to gel or the gel strength. The product is suitable for a wide variety of applications as a rheological additive.		

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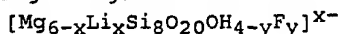
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Synthesis of smectite clay minerals

This invention relates to the synthesis of smectite clay minerals such as hectorite and more particularly to a method of controlling the synthesis to achieve particular product and processing characteristics.

Hectorite is a clay mineral which occurs naturally at several locations in the United States notably at Hector, California. Hectorite is a layered swelling trioctahedral magnesium silicate mineral which has a smectite type structure and having the general formula



in which x may have a value of from 0 to 1.2, y may have a value of from 0 to less than 4 and the overall negative lattice charge is balanced by cations. The composition and the rheological and other physical properties of this naturally occurring mineral may be somewhat variable and to avoid this, and to produce a material having relatively improved rheological properties, processes for the synthesis of hectorite-type materials have been developed. Other smectites such as saponite and montmorillonite have also been synthesised. The structures of smectites and of the individual smectite-type minerals identified above may be readily identified by X-ray diffraction techniques.

Very many of the hectorite syntheses have in common the precipitation of silica under basic conditions. Neumann, for example, in United States Patents No. 3586478 and 3671190 teaches the co-precipitation of magnesium and silicon values corresponding to the hectorite composition from a solution of a water soluble magnesium salt such as

magnesium sulphate or magnesium chloride, sodium silicate, a base such as sodium carbonate or hydroxide and, if appropriate, lithium and fluorine compounds and the treatment of the precipitate under hydrothermal and preferably elevated pressure conditions to achieve crystallisation with the formation of a hectorite structure. Neumann later disclosed in United States Patent No 4049780 a variation in the process comprising precipitating silicon values onto a preformed suspension of a water-insoluble magnesium compound. Further development of hectorite syntheses involved variation of the materials used. The use of partially or wholly degraded natural materials as a source of a proportion of the magnesium and/or silicon values was disclosed in, for example, United States patent No. 3954943. United States Patent No. 4054537 disclosed the inclusion of silica in sol form and Japanese Patent Publication No. 61-12848 disclosed its inclusion in the form of silicic acid. German Patent No. 3934473 disclosed the use of sodium bicarbonate as the base used to achieve precipitation. The use of pressure in the precipitation and crystallisation stages was disclosed in European Patent No. 88372. The patent disclosures listed above represent a limited selection of the art relating to hectorite synthesis and are quoted for illustrative purposes only.

Despite the considerable amount of research which has been conducted on hectorite syntheses, resulting in sometimes excellent laboratory scale preparations, the process has remained somewhat unpredictable on pilot or plant scale production in that some properties of the product may vary, apparently inexplicably from batch to batch. The present invention relates to a method for the control of the hectorite synthesis process with a view to reducing the variability of product and to improving certain properties thereof in aqueous dispersion.

The invention is based on the new information that there is a relationship between the process pH and at least some properties which affect the utility of the product.

Although broad pH ranges have been disclosed previously in a general context the present invention gives a new ability to control the character of the product and its consistency from batch to batch.

The effect of the suitable control of pH in the manufacture of a single batch or of successive batches of synthetic hectorite is reflected in one or more of the product features of increased dispersibility, optical clarity when dispersed in aqueous media, in time to gel and gel strength in such media, and in the washing ability of the product. While the first four properties are important to users of the product the last property is of great importance to the economics of the production process as is the ability to improve product consistency from batch to batch. The references herein to an aqueous media include reference to mixed aqueous/organic media unless the context otherwise requires. It is also envisaged that the product of the invention will give improvements in derivatised hectorites such as ion-exchanged hectorites which may suitably be organo-onium exchanged hectorites destined for dispersion in organic media. The present invention is described herein with particular reference to batch processes which are usually practised in the area of clay synthesis, possible due to the relatively lengthy pressure stage involved. However the principles of the invention are equally applicable to continuous processing.

United States Patent No. 3887454, which relates to the preparation of certain clay-like minerals which are structurally different to hectorite in that they are dioctahedral instead of trioctahedral, discloses the preparation of an aqueous slurry of a mixture of hydrous silica, hydrous alumina, hydrous magnesia and fluoride, the ageing of the slurry and, after ageing and before hydrothermal treatment at elevated temperature and autogenous pressure, the adjustment of the pH to from 7.0 to 10.5. The process is exemplified on a laboratory scale using pH values of 10.3 or 9.9. The product is intended for

use as a catalyst and its rheological properties are not considered.

Japanese Patent Publication No. 61-275126 describes a process for the synthesis of a modified synthetic hectorite in which 0.5% to 15% molar of the silicate fraction is substituted by alumina by direct treatment of an activated aluminosilicate solid product, a magnesia component and a compound or compounds comprising alkali metal and fluorine ions in stoichiometric proportions in an autoclave. The pH of the treatment mixture is advisably 8 to 11 especially 8.5 to 10. The process is exemplified on a laboratory scale only.

The present invention provides a process for the synthesis of a smectite type mineral such as hectorite comprising the formation of a solid reaction product containing the magnesium and silicon values of the hectorite by the precipitation of at least a proportion of the said values under basic conditions to form a precursor and the subsequent treatment of the said precursor under hydrothermal conditions to achieve crystallisation of a product having a hectorite structure with subsequent separation and washing of that product the process being characterised in that the pH under which the precipitation is conducted is controlled to improve processing or performance characteristics of the product. Preferably the reaction mixture containing the solid reaction product is initially hydrothermally treated at a temperature of from 60°C to below 160°C, for example, very conveniently, at reflux temperature under atmospheric pressure for, for example, 0.5 to 4 hours before hydrothermal pressure treatment. The hydrothermal pressure treatment may be conducted under the usual conditions for this technique for example under the autogenous pressure developed at a temperature of from 160°C to 300°C for, for example from 2 hours to 6 hours.

The present invention will be described hereafter with particular reference to hectorite, to which any specific

processing teachings hereafter will apply but the general principles of the teaching, as expressed in the preceding paragraph are equally applicable to the similar synthesis of other smectite minerals.

There is inherent scope for an appreciable variation in pH from batch to batch in normal plant operation of the hectorite synthesis process. By way of example, magnesium sulphate heptahydrate, a commonly used reactant in hectorite synthesis, may give aqueous solutions varying in pH by over 1. Samples of this chemical, taken from 18 different batches obtained commercially, gave pH values of ranging from 7.49 to 6.24. Samples of sodium silicate, while ostensibly the same product, may vary slightly in  $\text{Na}_2\text{O};\text{SiO}_2$  ratio and can give solutions having pH values ranging from for example 10.55 to 12.19 or from 11.59 to 11.98. The quantity and concentration of base added to achieve precipitation is subject to slight variation of quantity and concentration in normal plant operation. These effects, and others which will readily be apparent to those experienced in clay synthesis, can either cancel or aggravate each other in a random manner and, if the latter is the case, pH variations may be quite sufficient to cause departure from the area within which good product gel times are obtained.

According to a preferred aspect of the present invention the precipitation pH is controlled at from 7.5 to 9.0 with the qualification that the end points of this range may vary slightly, for example up to about  $\pm 0.25$ , depending on the precise synthesis conditions. The effect of this control on the time to gel, and on other product and processing characteristics of the product is quite dramatic. It has been found for example that at a precipitation pH of about 7.0 or slightly above the product will not gel and that at a precipitation pH of above about 9 a product is obtained which does not disperse completely and gives very poor gel times. At a precipitation pH of about 9.7 to about 10 a product of relatively poor although not bad gelling properties may be produced. This is within the invention

although it is not a preferred feature because it is difficult to control plant scale processes within such a narrow pH range and because of the sub-optimal effect of the invention within this pH area.

The control of process pH required by the present invention may be achieved by alternative means. The pH characteristics of the individual reactants may be monitored and the hectorite synthesis reactant mixture may be initially formed, with any required additional acid or base, to give the correct pH. Preferably, the reaction mixture is made up in the usual manner, and the pH of the reaction mixture is maintained and corrected at this stage before any elevated temperature treatment of the reaction mixture. It is also possible to delay the pH control until after an initial normal pressure hydrothermal treatment, e.g. by reflux, but before the reactant mixture, now containing precipitated and possibly partly crystallised product, is subjected to pressure hydrothermal treatment.

The pH is adjusted using a suitable reagent which will not interfere with the process, either a suitable acid such as  $\text{H}_2\text{SO}_4$  or HF or  $\text{HNO}_3$  or a suitable base such as NaOH or  $\text{NH}_4\text{OH}$  or other suitable acidic or alkaline material. While any concentration of acid may be used it is preferred not to add an acid of concentration above 80% w/w directly to the reaction mixture since this may affect the product in contact with the added acid before it is diluted by the body of the reaction mixture. It is also preferred not to add unduly dilute acid, e.g. below about 5% w/w to the reaction mixture since this would cause undue dilution of the entire reaction mixture possibly resulting in an alteration of the dynamics of the hectorite formation process. Preferably the acid is added at a concentration of from 5% to 50% w/w to the reaction mixture. The same considerations and numerical limitations apply to the addition of base.

The invention will now be illustrated by reference to the following examples of specific embodiments thereof.



In the Examples Figure I is a graph showing the variation of the gel time with the pH of a hectorite synthesis batch and Figure II is a graph showing the wash time of successive batches without (21 batches) and with (12 batches) pH control according to the invention.

#### Example 1

A number of samples of synthetic hectorite were produced under closely controlled different pH conditions.

The synthesis process was a standard one in which a solution of magnesium and lithium salts were precipitated by the addition of base and a sodium silicate solution was added to the suspension thus obtained to precipitate silicon values. After ageing the mixed precipitate under reflux to allow the reaction to go to completion it was subjected to treatment in an autoclave under a superatmospheric pressure and autogenous pressure until crystallisation had occurred, the product was filtered, washed free of salts with demineralised water to a given conductivity, dried and ground. The present invention is particularly applicable to synthetic hectorite produced by such a successive precipitation process, a magnesium compound being first precipitated and silicon values being precipitated onto it, for example the process described in US Patent No. 4049780 although it is not limited to this process.

The pH of the reaction mixture was controlled by the addition of sulphuric acid or sodium hydroxide and was determined by sampling the reaction mixture immediately after the addition of the sodium silicate i.e. before the initial hydrothermal treatment stage.

The time to gel of a 5% dispersion in water of the samples was determined under standard conditions and plotted against pH.

The product of two hectorite syntheses were made the subjects of two series of Examples (Series A and Series B) and the results as to the gel time of the product obtained from synthesis at different pH values are summarised in the graph attached hereto as Figure I.

It is seen from Figure I that the results of Series A and B exactly confirm each other up to pH 9.0 that, at a point which may vary between about 9.0 and about 9.24, the gelling performance of the product deteriorates suddenly and drastically and that at a pH of about 9.75 the product improves but at higher pH values again deteriorates.

Without control of pH to avoid the area between about 9.3 and about 9.75 or, preferably, between about 9.0 and 9.75 there is a likelihood of the production of batches of product having bad gelling characteristics.

#### Example II

Using the process described in the preceding example although on a larger scale a number of successive batches of hectorite were synthesised using a standard process. In the first 21 batches the process was operated without any attempt to control random variations in the pH. In the remaining batches acid ( $H_2SO_4$ ) was added to the formed reaction mixture before it was heated under reflux, to bring the pH to within the range 9.27 to 8.39.

The time to wash the product to a standard conductivity was noted and the speed of aqueous dispersion, the optical clarity of the dispersion, the time to gel and the gel strength of the product of each batch were measured all under standard conditions.

In Figure II the individual and average wash times are shown (in hours). It is seen that the variability in wash times greatly improved.

Typical average results obtained for non-pH controlled batches and batches produced according to the invention are as follows:

	Non-controlled Invention	
Wash time (hours)	9.6	6.3
Time to gel (mins)	6.1	3.2
Gel strength	31.5	41.0
Time to Disperse	20.8	18.1
Clarity of dispersal	12.0	9.4

This underlines the widespread nature of the improvements obtainable by the use of the present invention.

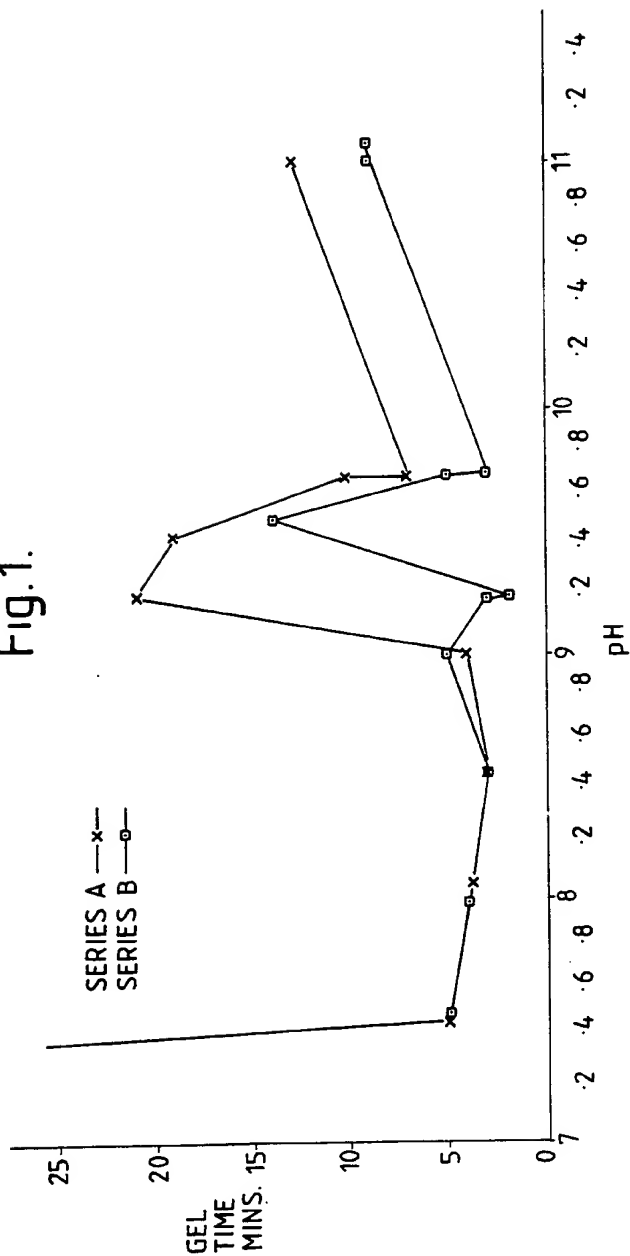
Claims

1. A process for the synthesis of a smectite type mineral comprising the formation of a solid reaction product containing the magnesium and silicon values of the mineral by the precipitation of at least a proportion of the said values under basic conditions to form a precursor and the subsequent treatment of the said precursor under hydrothermal conditions to achieve crystallisation of a product having the smectite structure the process being characterised in that the process pH is controlled to improve processing or performance characteristics of the hectorite product.
2. A process for the synthesis of hectorite comprising the formation of a solid reaction product containing the magnesium and silicon values of the hectorite by the precipitation of at least a proportion of the said values under basic conditions to form a precursor and the subsequent treatment of the said precursor under hydrothermal conditions the process being characterised in that the pH under which the precipitation is conducted is controlled to avoid pH values at which hectorite product having a poor gel time is synthesised.
3. A process as claimed in claim 1 or 2 wherein the process pH is controlled to improve the washing ability of the product or its dispersibility, optical clarity when dispersed, gelling speed or gel strength in aqueous media.
4. A process as claimed in claim 1 or 2 wherein the mineral has a hectorite structure and the process pH is controlled at from  $7.5 \pm 0.25$  to  $9.0 \pm 0.25$  or from 9.75 to 10.

5. A process as claimed in claim 1 or 2 wherein the pH is controlled at from  $7.5 \pm 0.25$  to below 9.3.
6. A process as claimed in any preceding claim wherein the process pH is controlled by the addition of a suitable reagent to the reaction mixture before hydrothermal treatment thereof.
7. A process as claimed in any preceding claim which comprises a multibatch process in which the process pH is controlled in at least some successive batches.
8. A process as claimed in claim 6 wherein the pH adjusted reaction mixture is subjected to an atmospheric pressure hydrothermal treatment at at least 60°C and for at least 0.5 hours and is subjected thereafter to a hydrothermal pressure treatment.
9. A process as claimed in any preceding claim wherein the pH is adjusted by the addition of sulphuric acid or nitric acid.
10. A process as claimed in any preceding claim wherein the pH is adjusted by the addition of a reagent having a concentration of from 5% w/w to 50% w/w.
11. A process as claimed in claim 1 or 2 and as specifically described in Example 1 or 2 wherein.
12. A synthetic smectite or hectorite whenever produced by a process as claimed in claim 1 or 2 herein.

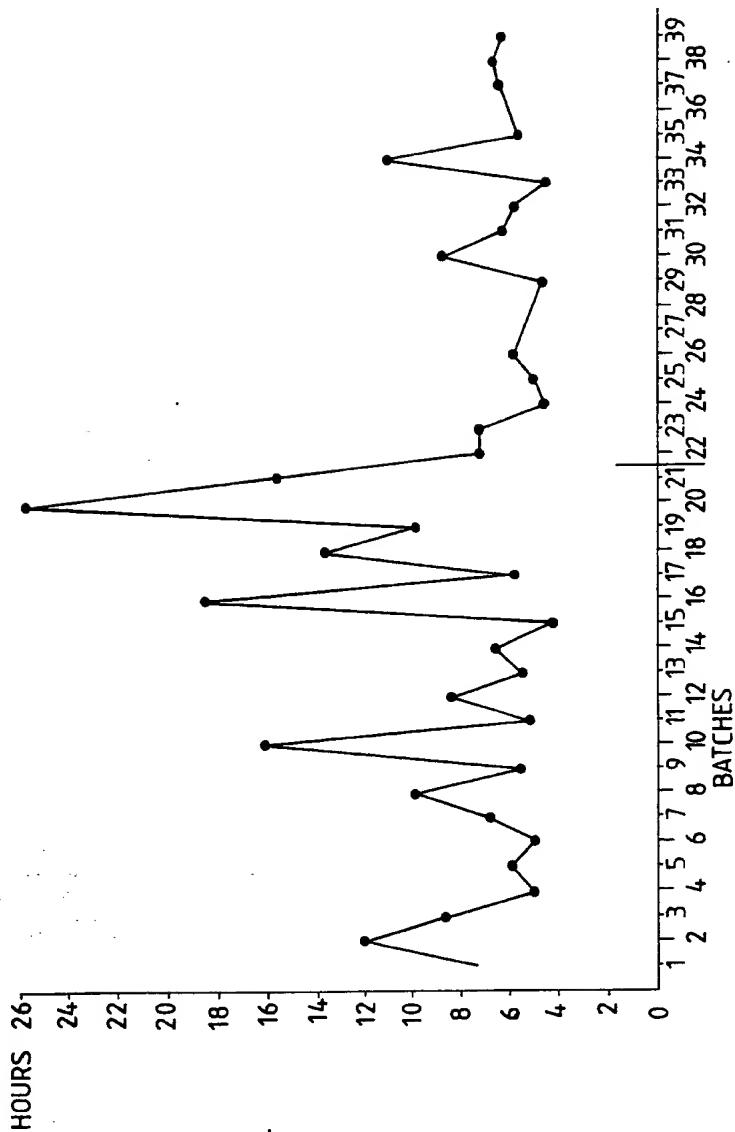
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Fig.1.



2/2

Fig. 2.



## INTERNATIONAL SEARCH REPORT

PCT/GB 92/02161

International Application No

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C01B33/20		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C01B	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	FR,A,1 565 348 (THE FULLERSIEARTH UNION LIMITED) 2 May 1969 see page 1, line 74 - page 2, line 22 see page 2, line 50 - line 53 see page 2, line 58 - line 62 ---	1-6, 11, 12
X	PATENT ABSTRACTS OF JAPAN vol. 14, no. 211 (C-0715)2 May 1990 & JP,A,20 48 410 (MIZUSAWA IND. CHEM LTD. ) 19 February 1990 see abstract -----	1, 3, 4, 11, 12
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<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search 29 JANUARY 1993		Date of Mailing of this International Search Report - 5. 02 93
International Searching Authority EUR PEAN PATENT OFFICE		Signature of Authorized Officer RIGONDAUD B.



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